UNITED STATES PATENT APPLICATION

of

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for

ONE-STEP CONSOLIDATION PROCESS FOR MANUFACTURING SOLID OXIDE FUEL CELLS

One-Step Consolidation Process for Manufacturing Solid Oxide Fuel Cells

This invention was made with Government Support under Contract Number DE-AC05-96OR22464 awarded by the Department of Energy. The Government has certain rights in this invention.

BACKGROUND OF THE INVENTION

The invention relates to the field of fuel cells and, in particular, to a low-cost fabrication technique for solid oxide fuel cells (SOFCs).

With the increasing emphasis towards more strict pollution control norms, the focus has shifted onto fuel cells as a source of energy. Higher efficiency, higher specific energy density, and reduced emission of pollutants such as SO_2, NO_2, and CO_2 make these devices a potent replacement for traditional means of generating power. In particular, solid oxide fuel cells seem the most promising technique for power generation.

Solid Oxide Fuel Cell (SOFC): SOFCs provide a very attractive and versatile means of efficiently converting chemical energy to electrical energy from a wide variety of fossil fuels with much lower environmental impact than conventional power generation systems such as those based on gas turbines. A schematic of an operating SOFC with reformed fossil (hydrocarbon) fuel is shown in Figure 1.

Figure 1 illustrates SOFC **100** which converts chemical energy from a variety of fossil fuels to electrical energy. SOFC **100** comprises a porous cathode **102**, a porous anode **104**, and a solid electrolyte **106**. Anode **104** and cathode **106** provide a voltage source **108**, wherein anode **104** oxidizes hydrogen in the fuel and cathode **106** reduces oxygen gas in air.

Figure 2 illustrates a fuel cell stack **200** with multiple cells. A series of stacked repeating cells with plate separators provides the multiple cell structure. The repeating cells comprise, sequentially, an end plate **202**, anode **204**, electrolyte matrix **206**, cathode **208**, and bipolar separator plate **210**. Current, oxidant and fuel flows are shown for end/ separator plates.

Electrical power generation systems based on SOFCs have many advantages: high power generation efficiency since chemical energy is directly converted into electrical energy and there is negligible transmission and distribution losses; cogeneration capability, especially if they are operated at above atmospheric pressures, since the product gases (steam) have a sufficiently high heat content; capability of operating on a wide variety of hydrocarbon fuels and generating much lower NO_x and SO_x levels since oxygen and hydrogen are electrochemically reacted; ability to internally reform hydrocarbon fuels because of the elevated operating temperature; high power-to-weight ratio since the fuel cell components are made of light-weight and relatively thin ceramic materials; flexibility in citing due to its lower environmental impact and noise-less operation; lower manufacturing time since the units are modular in nature and can be assembled on site; solid-state structures that can be easily transported; and wide range of applications that include stationary, transportation and military use.

The most successful state-of-the-art high-temperature SOFCs are manufactured by Siemens-Westinghouse. They operate at 900-1100^{0}C, with fuel utilization of 80-90%, and power density in the range of 0.2-0.5W/cm^2. The anode, electrolyte, cathode and interconnect materials are Ni-ZrO_2 cermet (electronic conductor), yttria-stabilized zirconia (oxygen-ion conductor), A-site (Sr) doped lanthanum manganite (electronic conductor), and A-site (Mg) doped lanthanum chromite (electronic conductor), respectively. The electrodes (anode and cathode) are 30-40%

porous and permit molecular diffusion of gases, and the electrolyte and interconnect are dense. The cathode (1-2 mm thick) is fabricated by green extrusion followed by sintering, the electrolyte (20-40 μm thick) by the electrochemical vapor deposition (EVD) process, the anode (100-150 μm thick) by slurry coating followed by sintering or EVD fixing, and the interconnect (50-100 μm thick) by a plasma-spray process. The cost of producing fuel-cell stacks with these batch-processed cells is estimated to plateau, with all foreseeable improvements, at $1500/kWe. This is still significantly (an order of magnitude) higher than their gas-turbine counterparts.

Research teams at various universities and industries are working on developing processes SOFCs to lower the manufacturing costs. Processing techniques being investigated include: tape calendering, tape casting, plasma-spray, sol-gel, colloidal processing, screen printing, etc. All these are batch processes requiring multiple heating, sometimes to temperatures over 1300^0C, and cooling steps that are expensive, time consuming, lowers productivity and are damaging to the individual cell components.

Fabrication techniques, like Electrochemical Vapor Deposition (EVD) for the electrolyte, and the processing technique, being batch type, contributes to the cost. The use of such exotic processes results in a complication of the complete cell manufacturing process along with the need for control over a number of parameters. Apart from the financial burden imposed, it also raises the difficulty of adapting such a system on a commercial scale.

The following references describe SOFCs in general, but they fail to provide for a single-step hot press operation for fabrication of either a single SOFC or a stack of SOFCs.

The European patent to Nishioka et al. (EP0552055A2), assigned to NGK Insulators, Ltd., provides for a process for producing solid oxide fuel cells. Disclosed is a process for

producing an SOFC with an air electrode and a fuel electrode provided on opposite surfaces of a solid electrolyte plate.

The German patent to Wersing et al. (DE4307967), assigned to Siemens AG, provides for an Integrated Ceramic High-Temperature Fuel Cell. Described is a method to form a high-temperature solid oxide fuel cell (SOFC) stack.

Whatever the precise merits, features and advantages of the above cited references, none of them achieve or fulfills the purposes of the present invention.

SUMMARY OF THE INVENTION

The present invention provides for a hot pressing or hot iso-static pressing to fabricate a planar SOFC in a single step. The process involves (a) identifying processing parameters to obtain densification/porosity associated with each individual part (anode, cathode, and electrolyte), (b) selecting a set of parameters to obtain an electrolyte having a density greater than 90% and a cathode/anode having porosity between 20-40%, and (c) hot pressing the entire fuel cell in a single step based on the selected parameters. Multiple SOFCs can be produced by the same single-step hot pressing process by pressing a linear repeating cell structure and associated separators.

The single-step hot pressing technique provides for an electronically conducting porous electrode structure with high gas permeability and a high electronic/ionic/gas contact area provided at the electrode/electrolyte interface and within the electrode, wherein such a structure also provides low gas-phase mass transfer resistance and low electrode-polarization resistance. Further porosity control in the electrode is obtained by using carbon powder/fiber or other pore formers.

By removing multiple batch processing and by simplifying the manufacturing process, considerable cost reduction is accomplished. Additionally, by optimizing the process, reduction in both the processing time and cost are obtained.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates a prior art schematic of a SOFC that converts chemical energy from a variety of fossil fuels to electrical energy.

Figure 2 illustrates a schematic of a multi-cell SOFC that converts chemical energy from a variety of fossil fuels to electrical energy.

Figure 3 illustrates an example of a hot press that can be used in conjunction with the present invention.

Figure 4 illustrates a schematic of hot pressing an entire planar fuel cell as per the present invention.

Figure 5 illustrates a schematic representation of high-temperature SOFC hot pressed with a wavy die and fractured cross section (inset) showing C:cathode, E: electrode, and A:anode.

Figure 6 illustrates polished dense (>95%) YSZ electrolyte-porous cathode interface of a sample hot pressed at $1,100^0$C.

Figure 7 illustrates an optimized structure of a hot pressed intermediate-temperature SOFC.

Figure 8 illustrates a cross-sectional SEM micrograph showing the nature of the porosity in the densified sample containing carbon powder.

Figure 9 illustrates the same sample after being oxidized at $1,000^0$C to try and burn out the carbon.

Figure 10 illustrates a cross-sectional SEM micrograph showing the densified sample containing carbon fibers.

Figure 11 illustrates the same sample shown in Figure 10 after oxidation to burn out the carbon.

DETAILED DESCRIPTION OF THE INVENTION

Although the present invention has been shown and described with respect to several preferred embodiments thereof, various changes, omissions and additions to the form and detail thereof, may be made therein, without departing from the spirit and scope of the invention.

It should be noted that although the specification discloses a one-step process for fabricating a solid oxide fuel cell, the present invention's process is envisioned to be encompass

the manufacture of a plurality of fuel cells in a one-step process. Thus, the number of SOFCs fabricated using the disclosed process should not be used to limit the scope of the present invention. Additionally, although examples in the specification describe consolidating the fuel cell structure via hot pressing, it should be noted that other alternatives and equivalents are also envisioned. For example, the hot pressing step of the present invention's process can be replaced by a hot iso-static press without departing from the scope of the present invention.

The present invention provides for a hot pressing or hot iso-static pressing to fabricate a planar SOFC in a single step. The process involves (a) identifying processing parameters to obtain densification/porosity associated with each individual part (anode, cathode, and electrolyte), (b) selecting a set of parameters to obtain an electrolyte having a density greater than 90% and a cathode/anode having porosity between 20-40%, and (c) hot pressing the entire fuel cell in a single step based on the selected parameters.

Figure 3 illustrates an example of a hot press **300** that can be used in conjunction with the present invention, wherein the hot press has a graphite-heating element. It should be noted that other equivalent presses are within the scope of the present invention. The powders are pre-processed by wet milling in methanol for approximately four hours for de-agglomeration and then dried at 600^0C for eight hours to remove the adsorbed species. The powder **302** is put into a die **304** which can be first coated with boron nitride slurry to prevent adhesion between the powder and the sleeve. The powder **302** is pre-pressed and then hot pressed under vacuum at a specified temperature and pressure. The displacement, applied pressure, and vacuum are recorded as a function of the temperature.

Figure 4 illustrates a schematic of the powdered layers which are pressed together (under heat) to produce SOFC **400**. The SOFC is manufactured using a pair of plungers **402, 410** and a plurality of heating elements **412, 414**. The SOFC is formed by consolidating, via a single step, an anode layer **404**, an electrolyte layer **406**, and a cathode layer **408**.

An illustrative embodiment comprising an entire high-temperature SOFC structure of dense yttria-stabilized zirconia (YSZ) electrolyte, porous strontium doped lanthanum manganite cathode and a porous nickel-zirconia cermet anode has been hot pressed in a single step with a wavy die as shown in Figure 5. It demonstrates that, the interfacial area between the electrode and the electrolyte can be increased through die design in order to reduce the effective charge-transfer resistance. By using a wavy die it is possible to shape the gas channels directly in the electrodes. However, straight and other shaped dies are within the scope of the present invention. In addition, it is evident to one skilled in the art that the interfaces between the components can be compositionally graded to decrease residual stresses arising during thermal cycling.

Figure 6 shows the polished interface between a porous electrode (cathode) and the YSZ electrolyte that was hot pressed at 1100^0C with 2,500 psi pressure for 30 minutes. The variation in density between the YSZ electrolyte (fully dense) and the electrodes (porous) is attained by controlling the particle size and distribution of the original powders. For example commercially available YSZ powders with a wide range of particle sizes, with mean diameters ranging from nano (<0.1 μm) to 1500 μm were investigated. It was established that YSZ could be densified to greater than 90% without interconnected porosity at temperature as low as 1000^0C and pressures in the 2500 psi range when the mean particle diameter of the starting powder was 5 μm and below. For those skilled in the art of PM (powder metallurgy) it should be evident that further

modifications in powder morphology and distribution, via milling, may yield even lower YSZ densification process parameters.

The present invention hot pressing process can also be used for one-step manufacturing of solid oxide fuel cell that operates at intermediate temperatures (600-800 degrees C). Figure 7 illustrates an example of an intermediate temperature solid oxide fuel cell **700** comprising a dense electrolyte **704**, porous anode **708**, and a porous cathode **702** based on lanthanum gallate ($La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ or LSGM), nickel-ceria ($Ce_{0.9}Y_{0.1}O_{2-x}$) cermet, and LSGM-lanthanum cobaltite ($La_{0.8}Sr_{0.2}CoO_3$, or LSC) composite, respectively. The cathode **702** and the anode **708** are about 20-40% porous (5-15 μm pores), and about 100 μm to 2 mm thick. On the other hand, the electrolyte **704** is about 5-20μm thick. The intermediate temperature SOFC **700** further comprises a layer **706** of particulate phases at the anode-electrolyte interface (Y_2O_3 Doped-CeO_2). These material choices meet the operational requirements of the intermediate-temperature SOFC. The development of the one-step hot pressing process would involve determining the range of hot-pressing parameters for the individual components and then identifying a common range of parameters to hot press the entire intermediate-temperature SOFC structure in one step. This can be done in an iterative manner by electrochemically, chemically, and mechanically evaluating the hot-pressed components and relating the process parameters to the respective structures and properties obtained. The processing parameters that need to be tailored would include: particle size and distribution in the starting powders, hot pressing environment, temperature, pressure and die design, interfacial composition, and relative amounts of the phases in the cermet anode and the composite cathode. The process can then be also used to press multiple cells at a time in order to assemble a fuel cell stack with metallic interconnects.

Additionally, porosity control can be further achieved by mixing the Sr doped $LaMnO_3$ powder with C powder (30% by volume), carbon fibers, corn starch, and/or functional equivalents. Figure 8 illustrates a cross-sectional SEM micrograph showing the nature of the porosity in the densified sample containing carbon powder. Figure 9 illustrates the same sample after being oxidized at $1,000^0$C to try and burn out the carbon. It should be noted that no carbon peaks were detected via XRD analysis. Figure 10 illustrates a cross-sectional SEM micrograph showing the densified sample containing carbon fibers. The sample showed no reaction between the parent matrix and the carbon fibers. Figure 11 illustrates the same sample after oxidation to try and burn out the carbon. However, it is to be noted that it is possible to obtain the desired porosity in the electrode structure by tailoring the powder size and distribution along with proper selection of the hot pressing load and temperature.

The process of the present invention offers many advantages, some of which are listed below:

(1) the disclosed process significantly lower the process cost;

(2) the disclosed process improves interfacial contact and lowers interfacial resistance;

(3) the disclosed process allows graded structures to be developed for lowering internal stresses during thermal cycling; and

(4) the disclosed process increases the gas-ionic-electronic contact area in the electrodes and lower electrode polarization losses.

What is claimed is: